Fuel Cells, Durability and Performance, 2006
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Durability of Advanced Electrocatalysts for PEM Fuel Cells

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Cabot Fuel Cells

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- New name, clear commitment to Fuel Cells commercialization
- Combining the expertise in carbon supports with electrocatalyst manufacturing
- New methods, new results!
    - Hydrogen-air FC & DMFC materials solutions
- Advanced electrocatalysts for Hydrogen Air Fuel Cells:
    - Low precious metal alloys
    - Oxidation resistant carbon supports
    - Modified carbon black supports for low humidity operation

Cabot Fuel Cell Materials Development

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Performance
mW/cm^2

Cost
gPt/kW; $/kW

Durability
5000 h

- **Low Precious Metal Alloy Electrocatalysts**
- **Advanced Carbon Supports**
- **Easy Handling for Inks Formulation**
- **Optimized Electrode Layers and MEA Structures**

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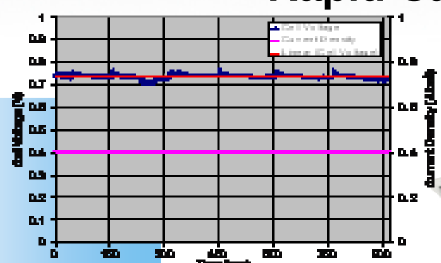
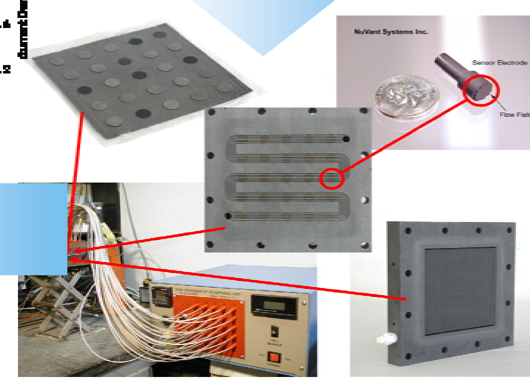
High Throughput Catalyst Discovery Platform is Key Element for Rapid Optimization of Complex Alloy Compositions

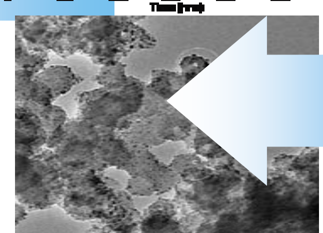
High Throughput Synthesis

Rapid Cathode Layer Fabrication





Rapid Screening in MEA Configuration



Electrochemical and Physical Characterization

High Volume Production

Two Fold Mass Activity Improvement Demonstrated by Ternary Pt- Alloy Supported Catalysts

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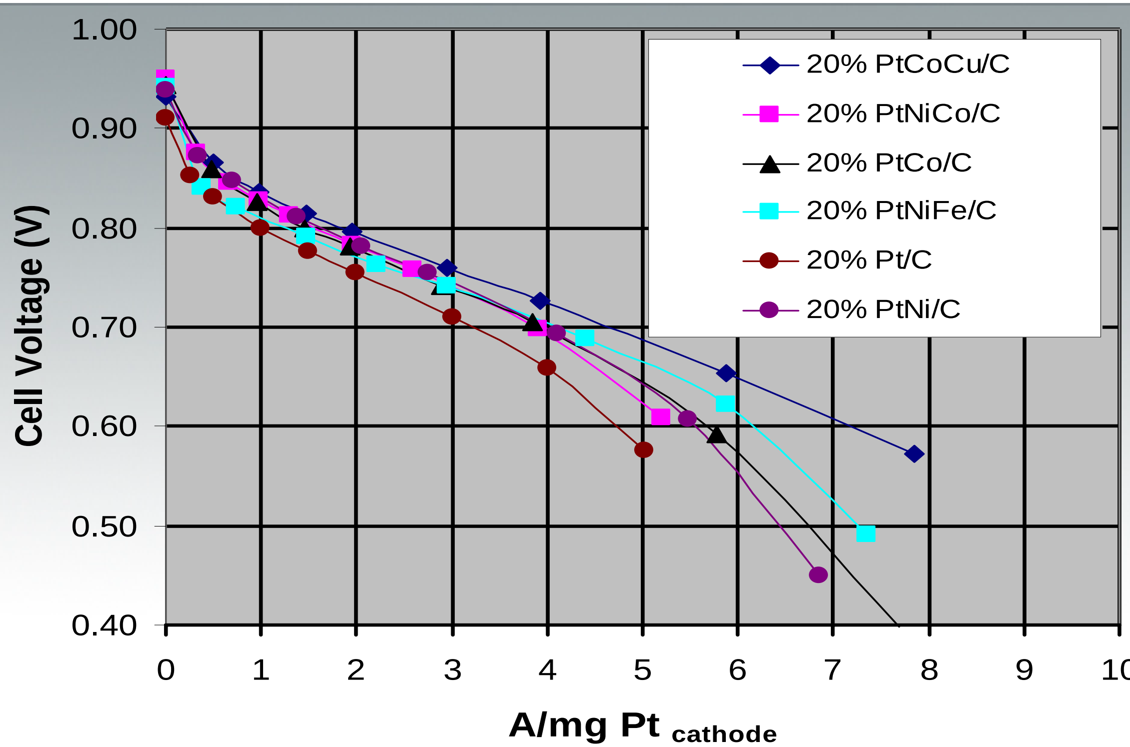
1	**PtCoCu**
2	**PtCoFe**
3	**PtFeCu**
4	**PtNiCu**
5	**PtNiFe**
6	**PtPdCu**
7	**PtPdCo**
8	PtPdFe
9	PtMnFe
10	PtPdMn
11	**PtNiCo**
12	PtCoAg
13	PtFeAg
14	PtNiAg
15	**PtPdNiCo**



Best Pt alloy compositions show up to 2 fold mass activity improvement in hydrogen air fuel cell

Test Conditions:

- **Non IR corrected, 50 cm^2 MEA, Nafion™ 112**
- **Loadings: Cathode: 0.2 mgM/cm^2, Anode: 0.05 mgPt/cm^2**
- **80ºC, 1.5 H_2/2.5 air at 1A/cm^2, 100% RH, 30 psig, 10min/point**

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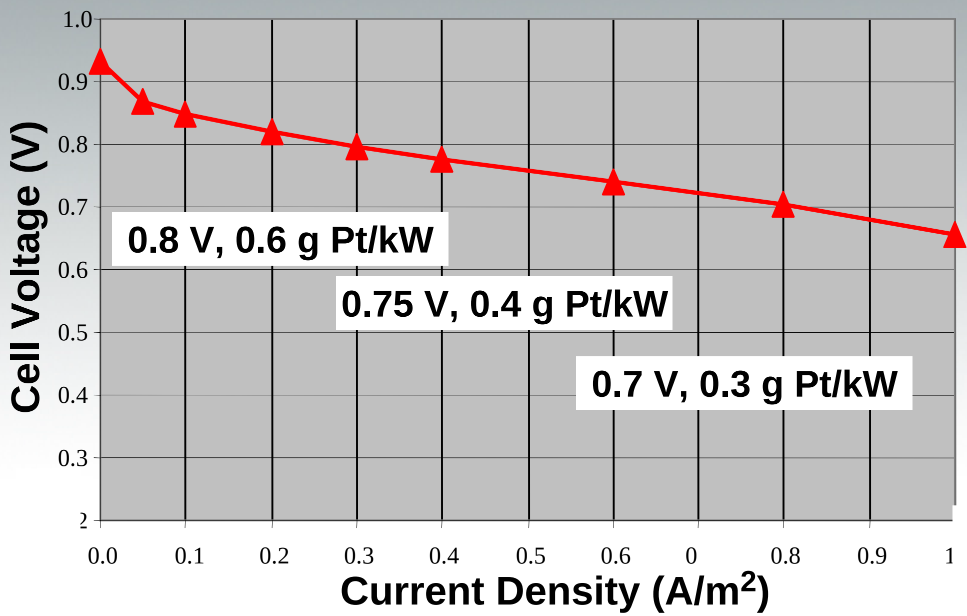
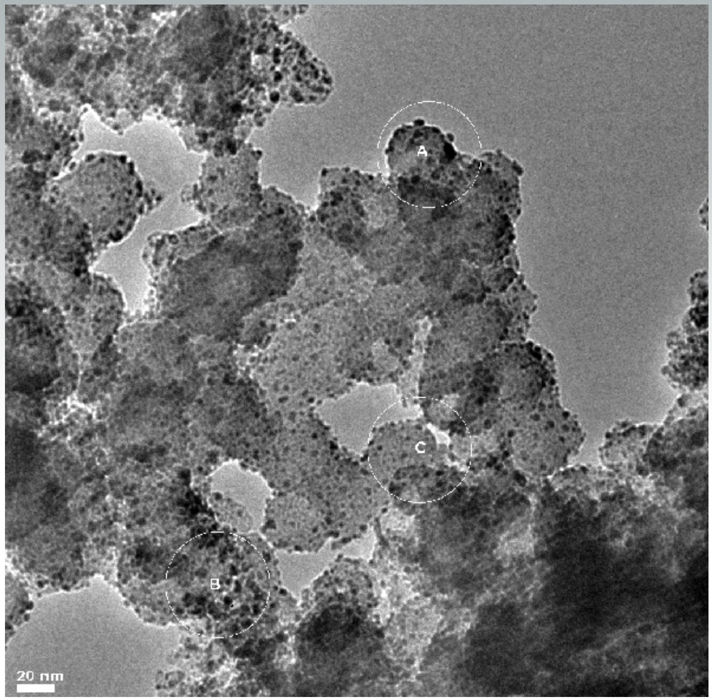
Superior MEA Performance at Low Precious Metal Loadings

Highly Dispersed Alloy Catalysts





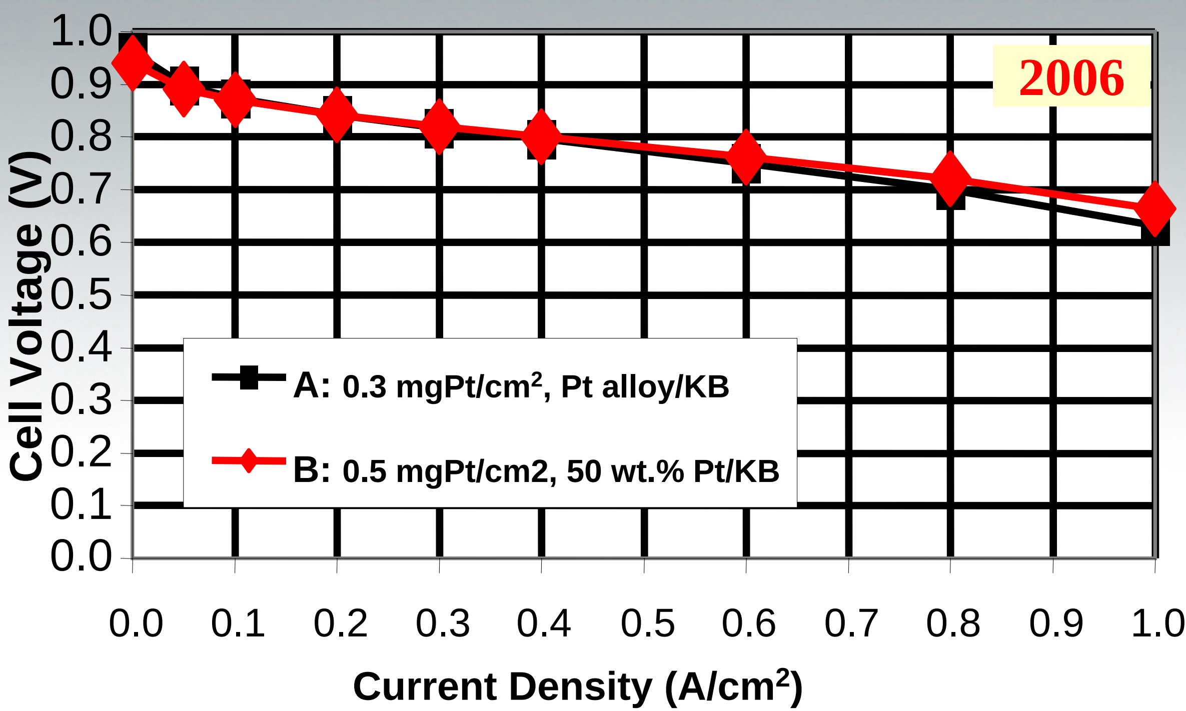
MEA loadings: 0.15 mg Pt/cm^2 total loading
Cathode: 0.1 mg Pt/cm^2; Anode: 0.05 mg Pt/cm^2

Pt (111): 40.36 (2θ); a: 3.87 Å
Particle size (XRD): 2.4 nm

Test Conditions:
- 50 cm^2, Nafion™ 112
- 80°C, 1.5 H_2/2.5 air at 1A/cm^2, 100% RH, 30 psig

10 min/point, Non IR corrected

High Absolute Performance Combined with Low Precious Metal Loadings



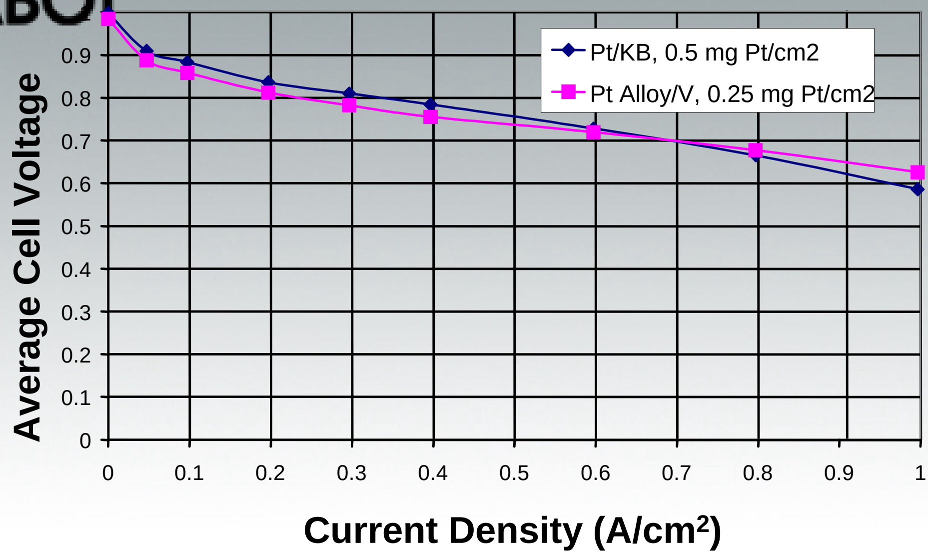
- ***High Metal Loading Catalyst on High Surface Area Carbon Support***
- ***Identical performance at approximately half of the Pt content***

Test Conditions:

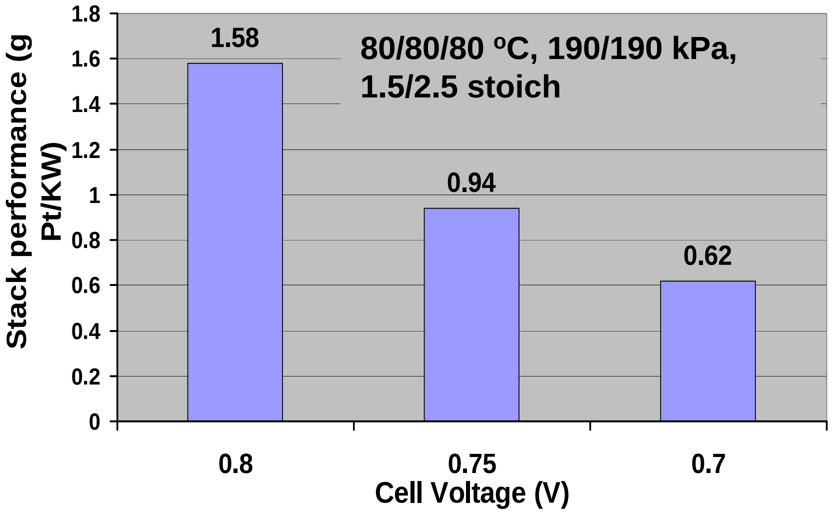
- **Non IR corrected 50 cm², Nafion™ 112, cathode: as listed; anode: 0.05 mgPt/cm²,**
- **80°C, 1.5 H_2/2.5 air at 1A/cm², 100% RH, 30 psig, 10 min/point**

- **At 0.8 V a power density of 0.32 W/cm² was achieved**
- **At 0.7 V approximately 0.56 W/cm² (total PM loading, anode plus cathode of 0.35 mgPt/cm²), which corresponds to approximately 0.6 gPt/kW.**
- **The corresponding value for Pt only catalyst at 0.7 V is approximately 0.9 gPt/kW**

Short Stack Testing Validates Alloy Catalysts Performance



- *Short stack evaluation completed by Hydrogenics Corporation*
- *0.6 gPt/kW demonstrated in a short stack at 0.7 V and stoich test conditions*

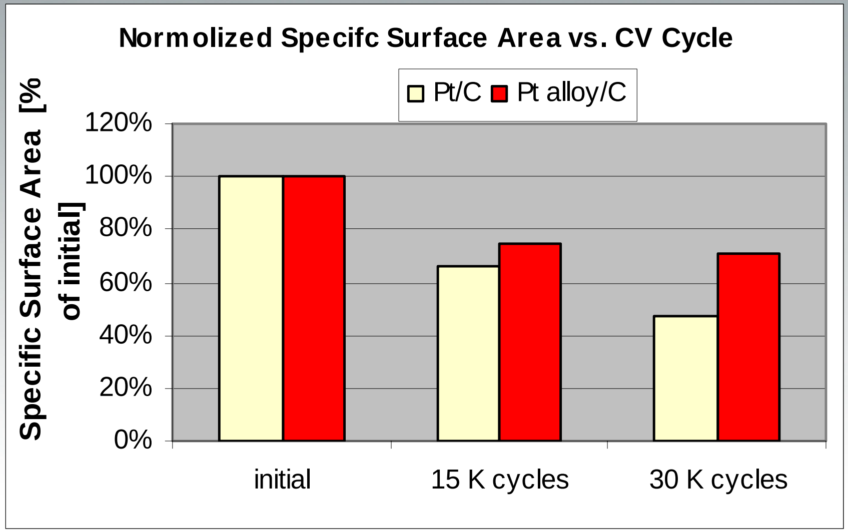


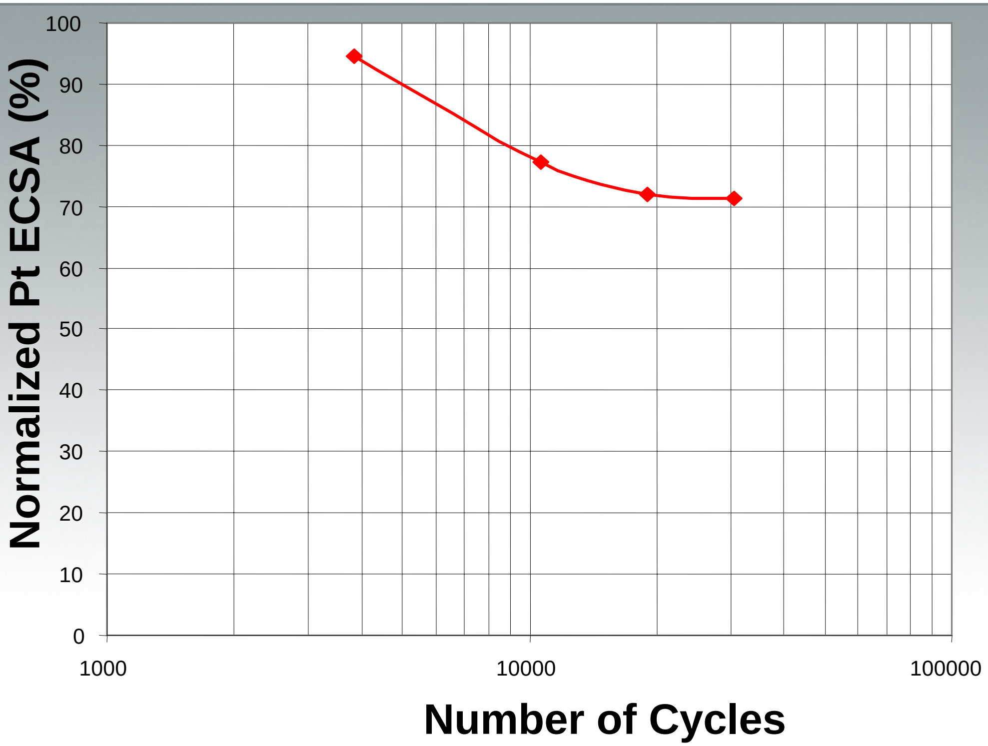
Stack Test Conditions:

- 5 cell, large area, Nafion™ 112 cathode: as listed; anode: 0.05 mgPt/cm²
- 80/80/80ºC, 55/55 kPa, 1.5/2.5 stoich
- 80/80/80ºC, 190/190 kPa, 1.5/2.5 stoich
- 80/80/64ºC, 175/175 kPa, 2/2.5 stoich

	Mass activity (A/mg Pt cathode)		Performance improvement (%)
	50% Pt/KB	Pt Alloy/V	
0.8V	0.67	0.95	42
0.75V	1.04	1.7	63
0.7V	1.37	2.75	100

Long-Term Durability Under Cycling Protocols





Test Conditions:

50 cm² MEA, cycling under H_2/air at 80°C and 100% RH between 0.7 and 0.9 V IR-free voltage (30 s hold at each potential) combined with periodical evaluation of the Pt surface area using cyclic voltammetry and performance.

Pt alloy catalyst shows 30% loss of surface area after 20 K cycles and no further loss is observed until 30K cycles !

Long-Term Durability Under After Cycling Protocols

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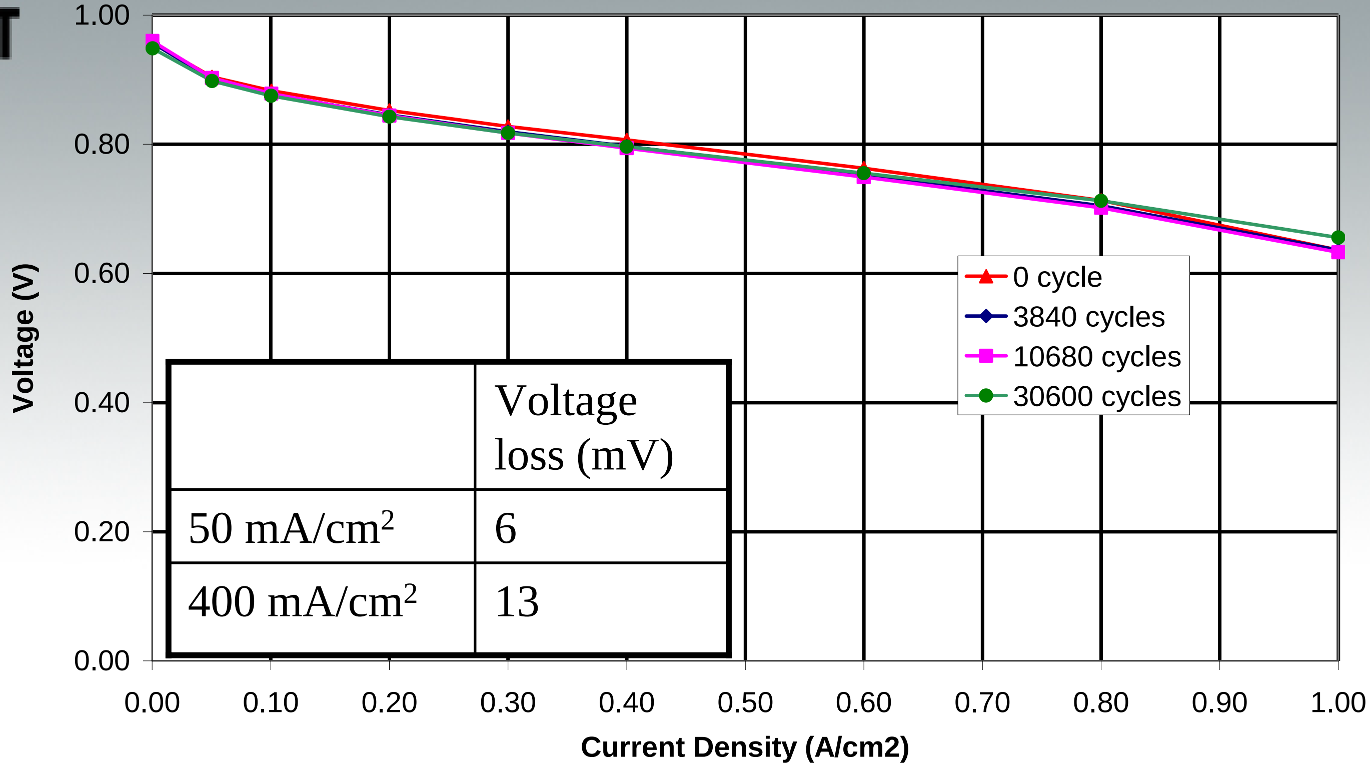

	Voltage loss (mV)
50 mA/cm^2	6
400 mA/cm^2	13

Test conditions:

- Single MEA 50 cm^2 test cell, Nafion 112, Cell temperature 80°C
- Anode/cathode constant flow rates = 510/2060 mL/min H_2/air (1.5H_2/ 2.5 air stoich at 1 A/cm^2)
- 30 psig pressure on both anode and cathode, 100% humidification of gases, 80C dew point

Ability to Control Carbon Support Properties

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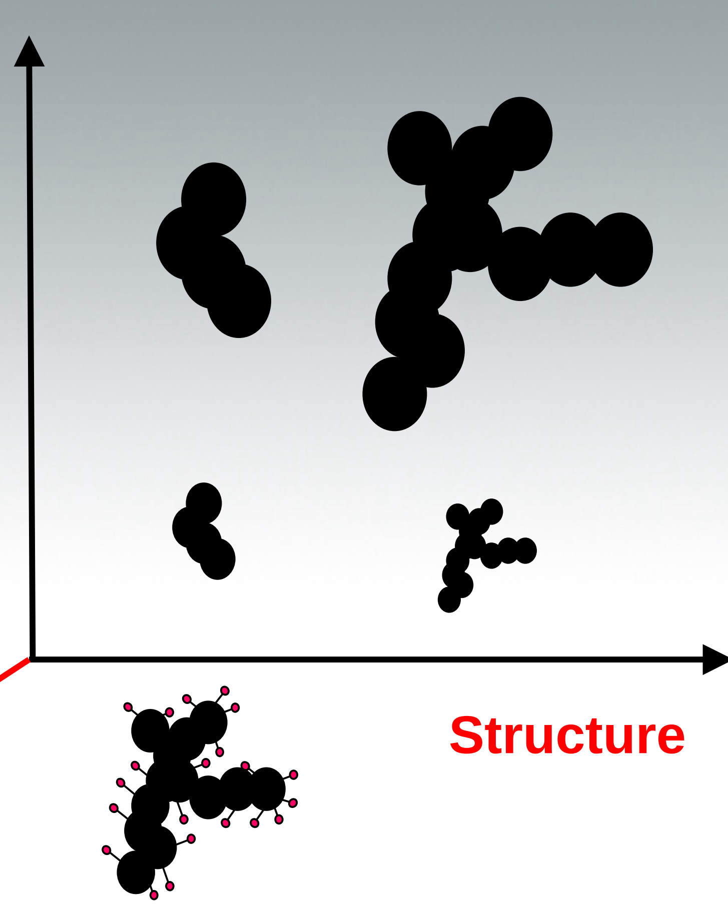
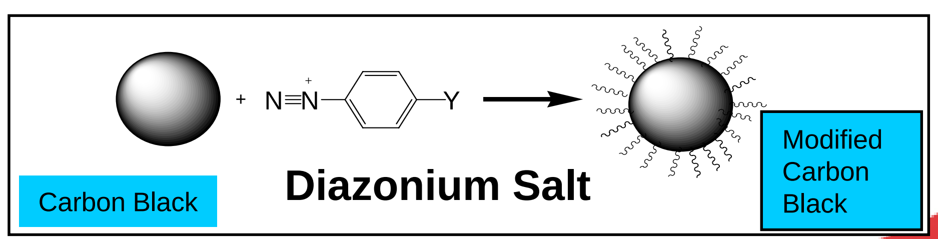
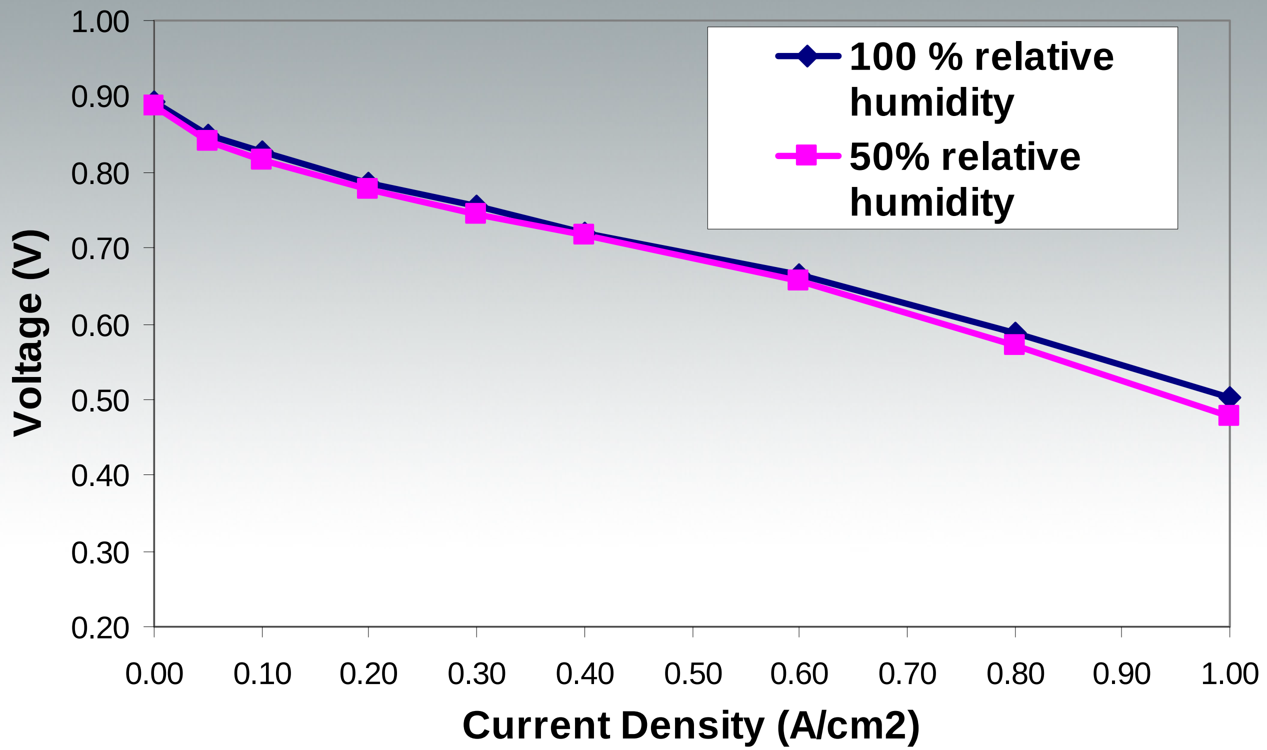
Combination of morphology control and surface modification allows for *rational design of carbon materials*

- Carbon black morphology can be controlled to design the length scale of gas and water transport channels
- Various degrees of carbon support graphitization can be achieved
- Carbon support surface chemistry can be modified





Surface Modification Enables Operation at Low Relative Humidity Conditions



- **100 % relative humidity test: flow stoich = 2.0 (A/C), cell temperature 80°C back pressure =10 psig (A/C), RH=100% (A/C)**
- **50 % relative humidity test: flow stoich = 2.0 (A/C), cell temperature 80°C back pressure =10 psig (A/C), RH=50%/50% (A/C)**

Long Term Performance Losses Related to Carbon Corrosion

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- **Carbon Support Durability is considered to be a major barrier for commercialization of automotive fuel cells**
- **Carbon corrosion is accelerated during start/ stop cycles and at high temperature operating conditions**
- **Type of performance losses related to carbon corrosion**
  - **Pt sintering due to loss of active phase/support interaction**
  - **Oxidation of carbon surface leads to layer flooding effects**
  - **Break down in carbon/carbon interface**
- **Conventional approaches to improving carbon durability lead to trade offs between durability, absolute performance and catalyst ink properties**

Long Term Performance Losses Related to Carbon Corrosion

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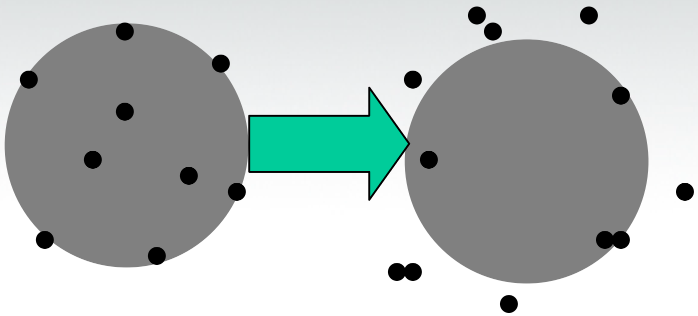
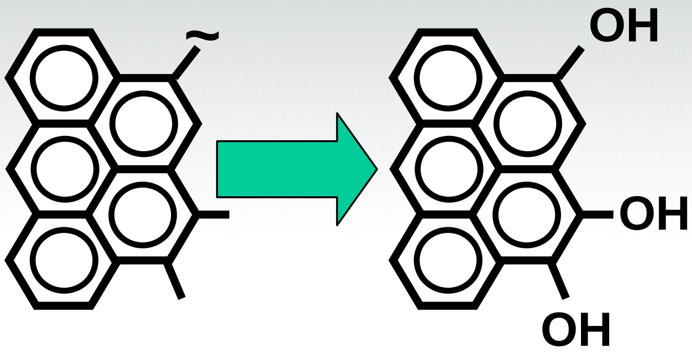
Kinetic Losses



- Sintering
- Pt particles move away from carbon surface (undercutting)
- Kinetic hindrance

Mass Transport Losses



- Surface oxides are formed during corrosion
- Hydrophilic in nature
- Flooding
- Prevents gas flow

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Long Term Performance Losses Related to Carbon Corrosion

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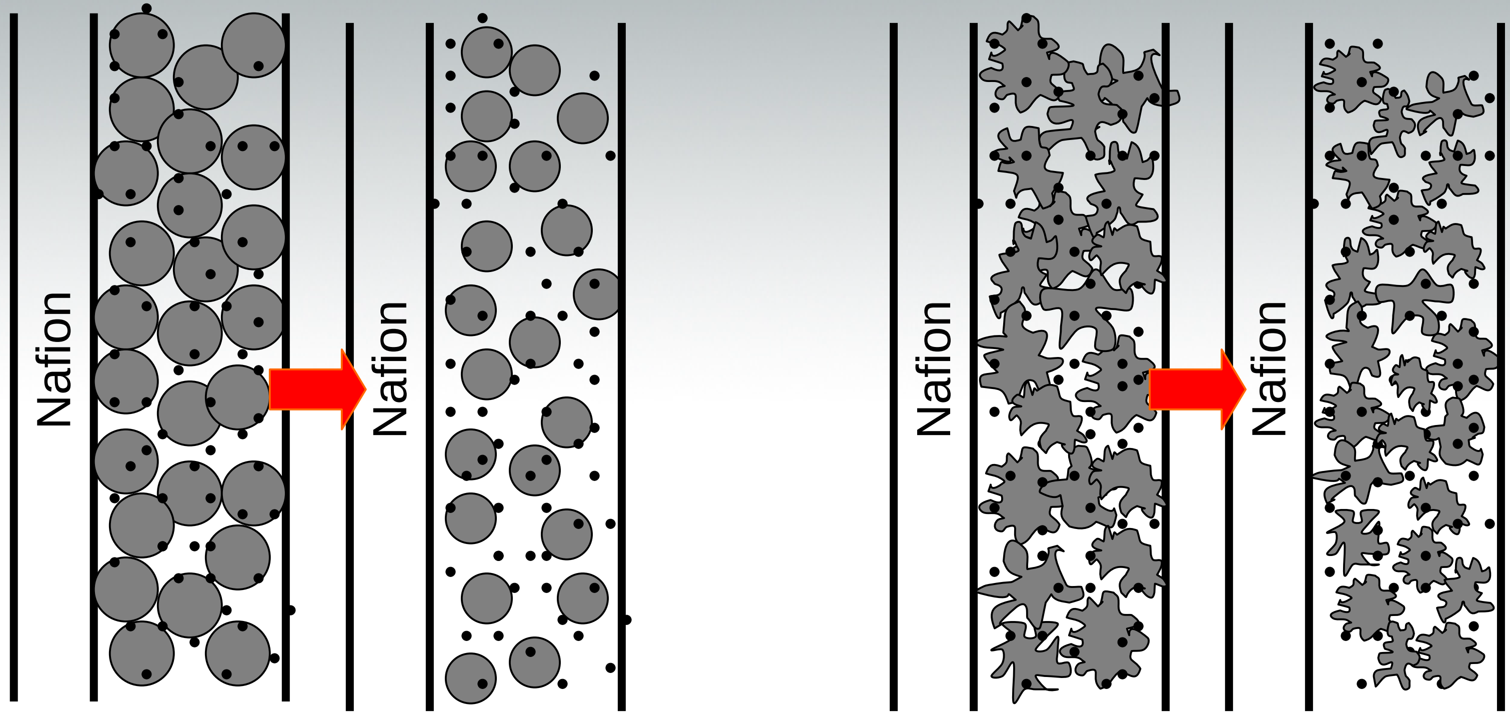
Ohmic Losses



Percolation effects in conductivity/connectivity of porous matrixes

Carbon Corrosion Analysis Approach

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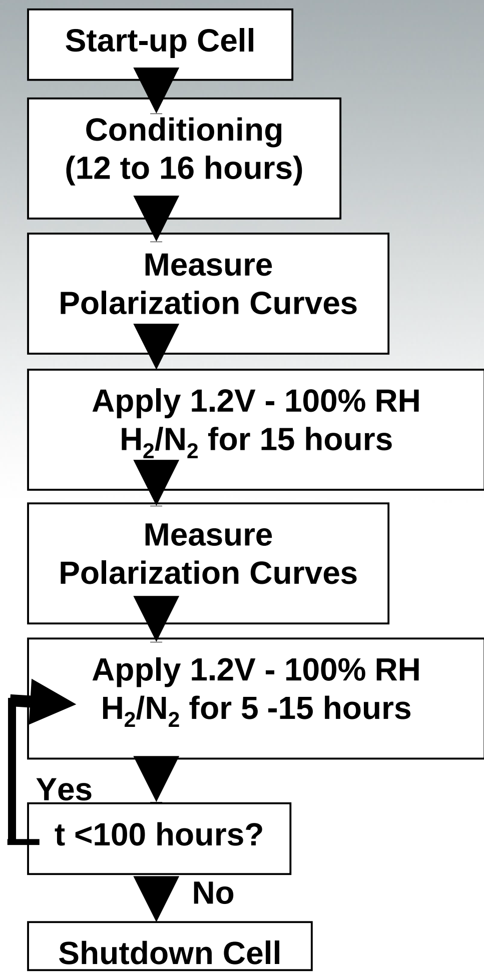

- **Investigate and evaluate the corrosive behavior of dispersed carbon blacks in low temperature fuel cell environment**

- **Corrosion resistance evaluation protocol adopted from GM/DOE**
  - **Polarization curves test conditions 80°C, stoich flows A/C = 3/3, 50% RH, 7 psig**

- **Study the effect of platinum loading, surface modification and morphology of the carbon blacks on the corrosive behavior of electrocatalysts.**

- **Goal – less than 30 mV loss at 1 A/cm^2 after 100 hrs corrosion test**

Severe Corrosion Losses with Standard Supports

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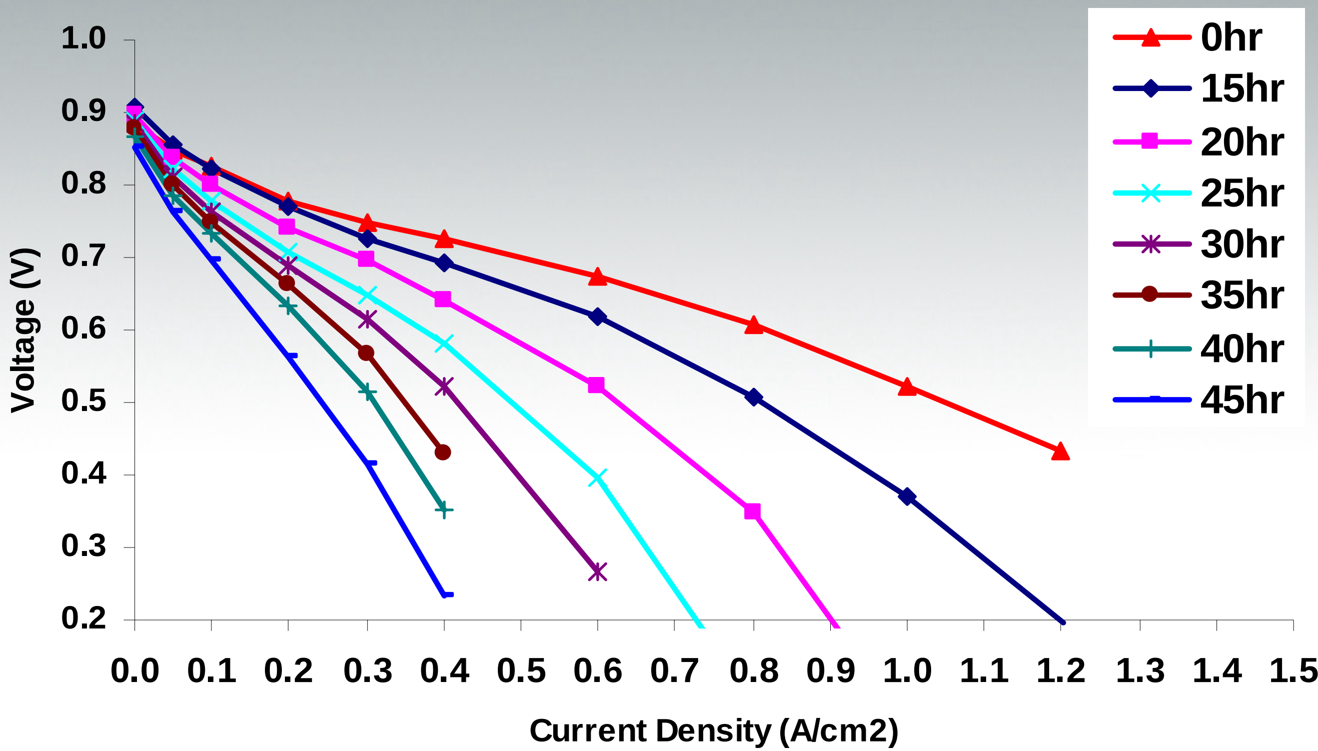
60% Pt / Ketjen Black



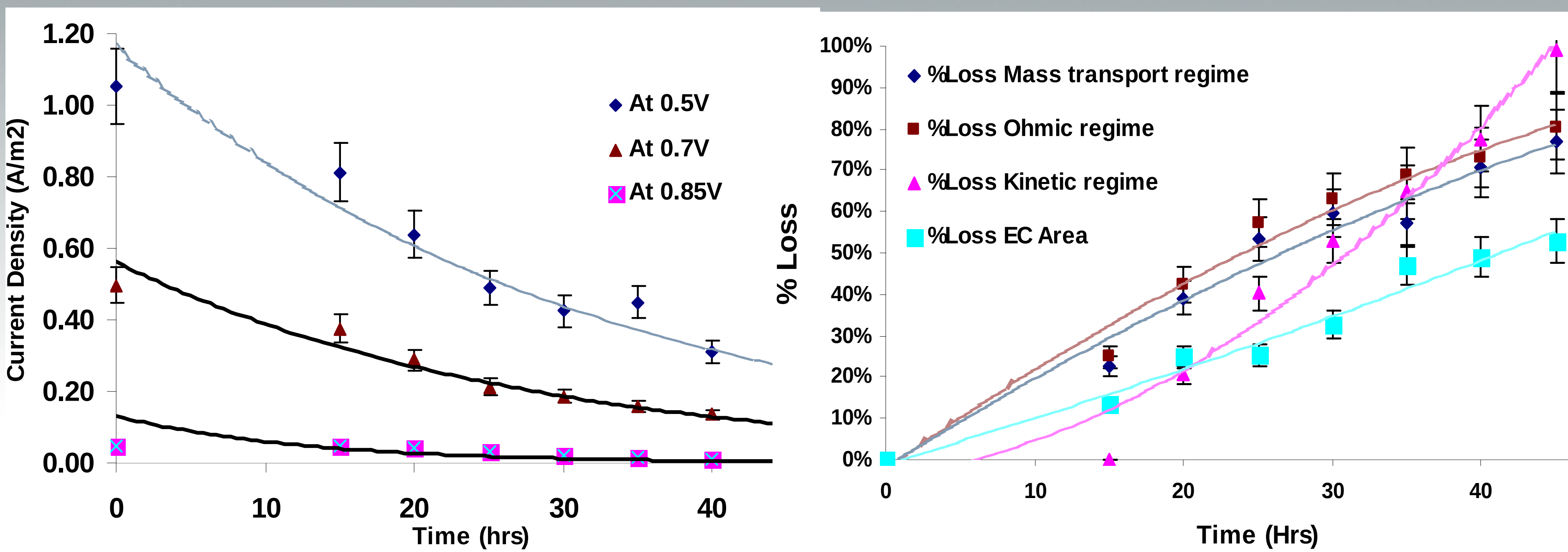
Polarization curves test conditions:

80/80/80°C, stoich flows A/C = 3/3, 50% RH, 7 psig

- **> 100mv loss at 1A/cm² only after 15hrs**
- **> 50% Loss in EC area after 45hrs of standard corrosion protocol**

Severe Corrosion Losses with Standard Supports

60% Pt / Ketjen Black



- > 70- 90 % Losses in kinetic, ohmic and mass transport regime
- > 50% Loss in EC Area after 45hrs of standard corrosion protocol

Surface Modification Effectively Enhances Carbon Corrosion Resistance

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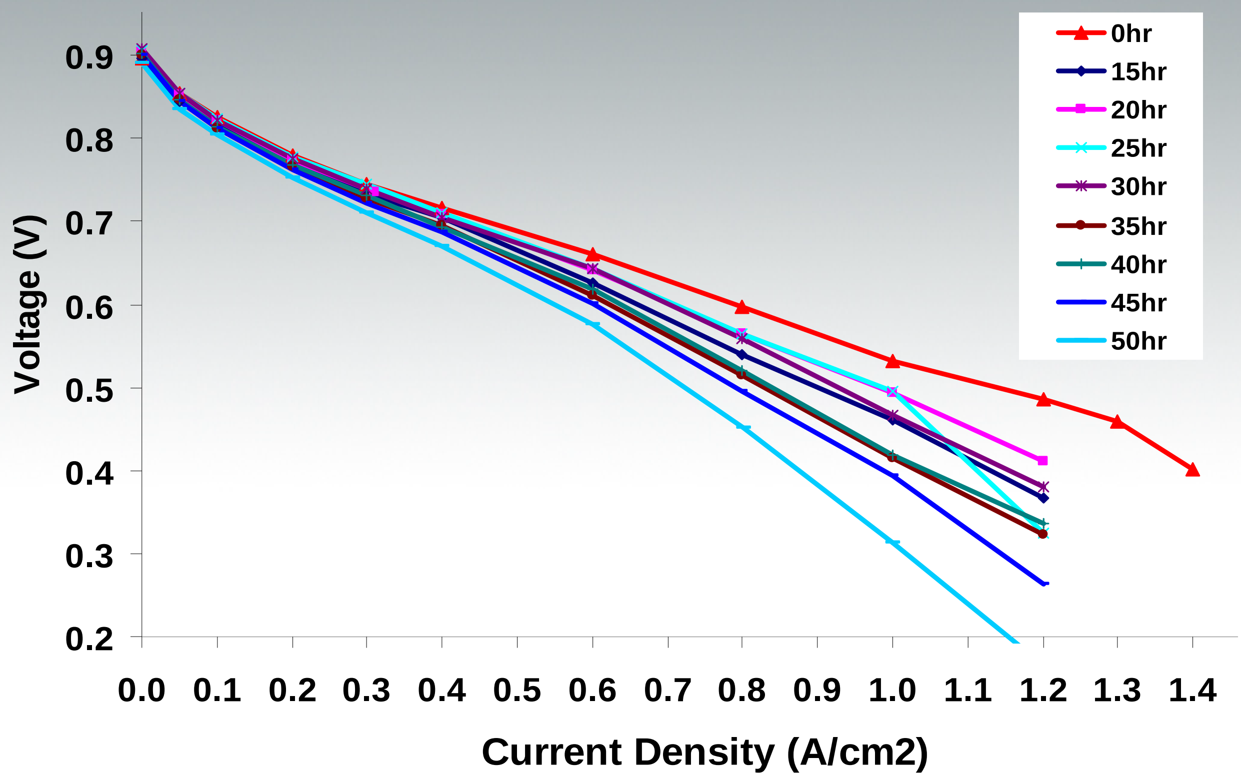
60% Pt / Modified Carbon Black (MCB)



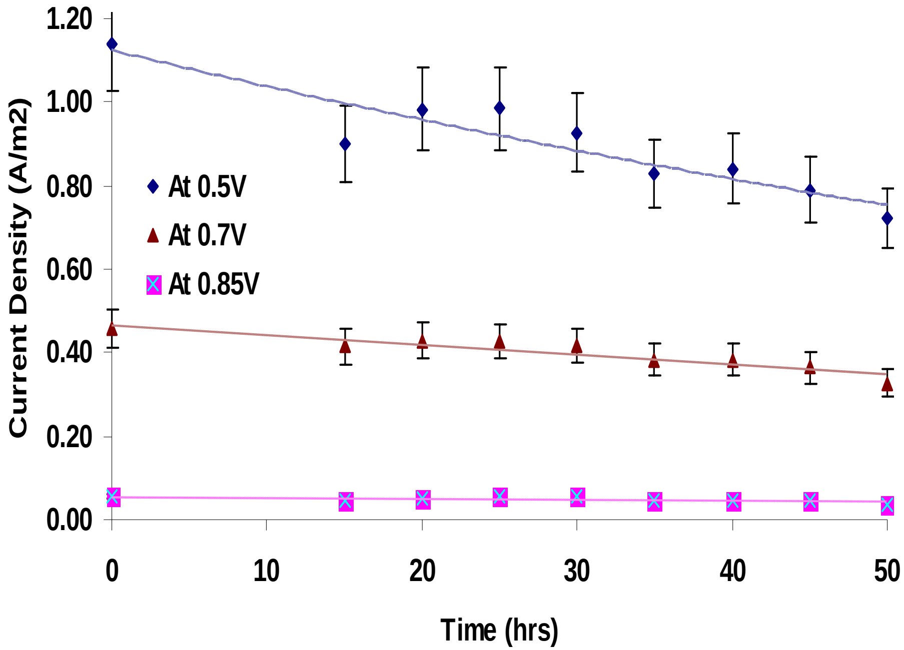
Polarization curves test conditions:

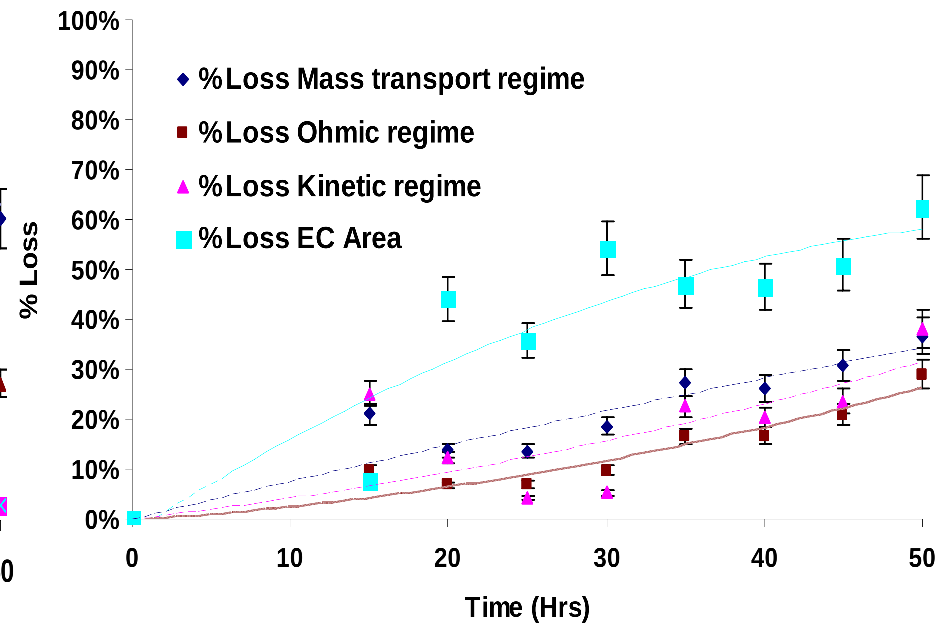
80°C, stoich flows
A/C = 3/3, 50% RH,
7 psig

- > 100mV Loss at 1A/cm^2 after 50hrs, ~3 fold improvement
- Improvement is related to the coverage of functional groups on carbon surface
- Functional groups stabilize the carbon surface

Surface Modification Effectively Enhances Carbon Corrosion Resistance

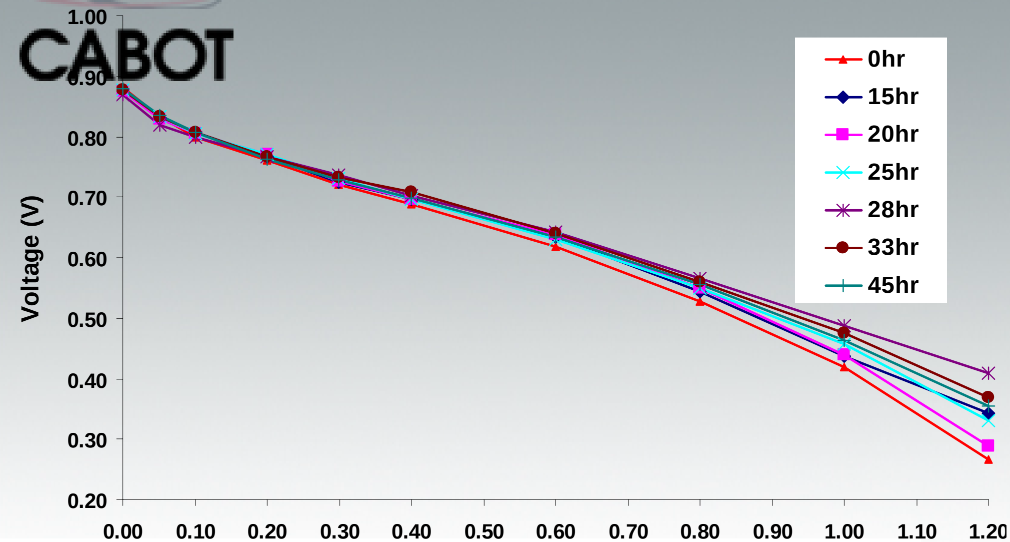
60% Pt / Modified Carbon Black (MCB)



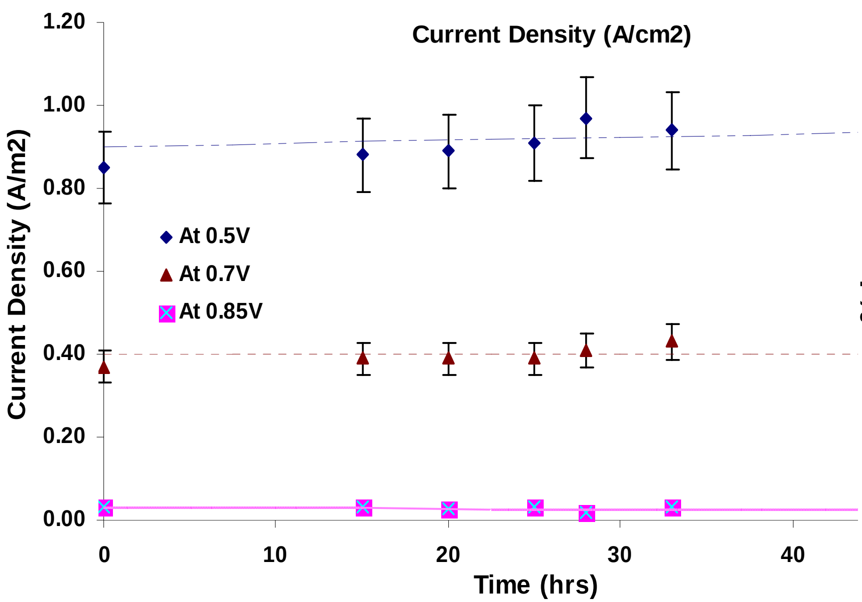


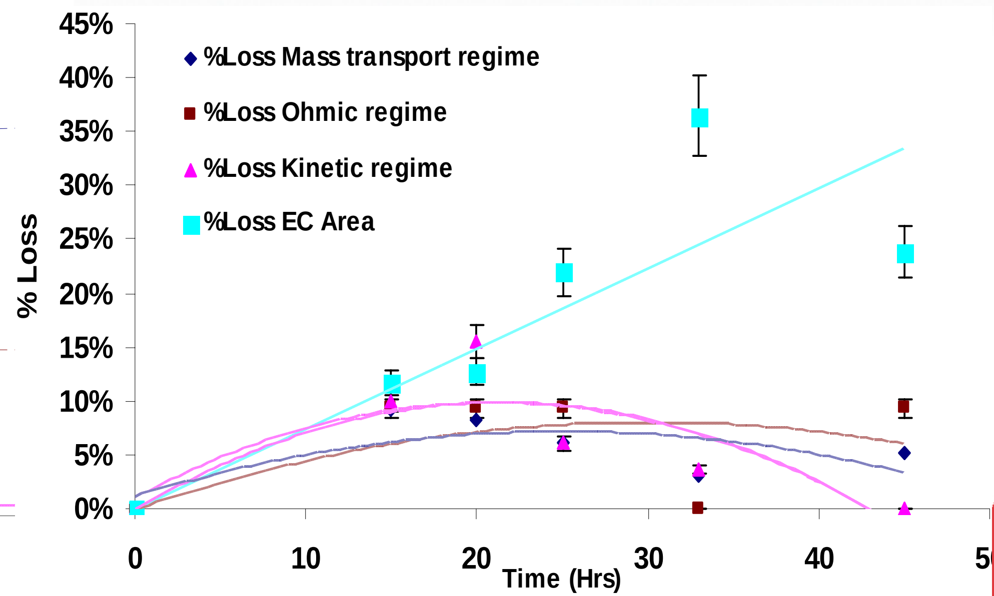
- < 35 % Losses in kinetic, ohmic and mass transport regimes
- < 60% Loss in EC Area after 50hrs of standard corrosion protocol
- Relative performance loss observed is relatively low compared to loss in EC Area

Superior Corrosion Resistance with Experimental Cabot Carbon Support



- ~ No Loss at 1A/cm^2 after 45hrs
- < 10 % change in performance in kinetic, ohmic and mass transport regimes
- A maximum of 25% loss in EC area is observed after 45 hours.
- Relative performance loss observed is very low compared to loss in EC Area





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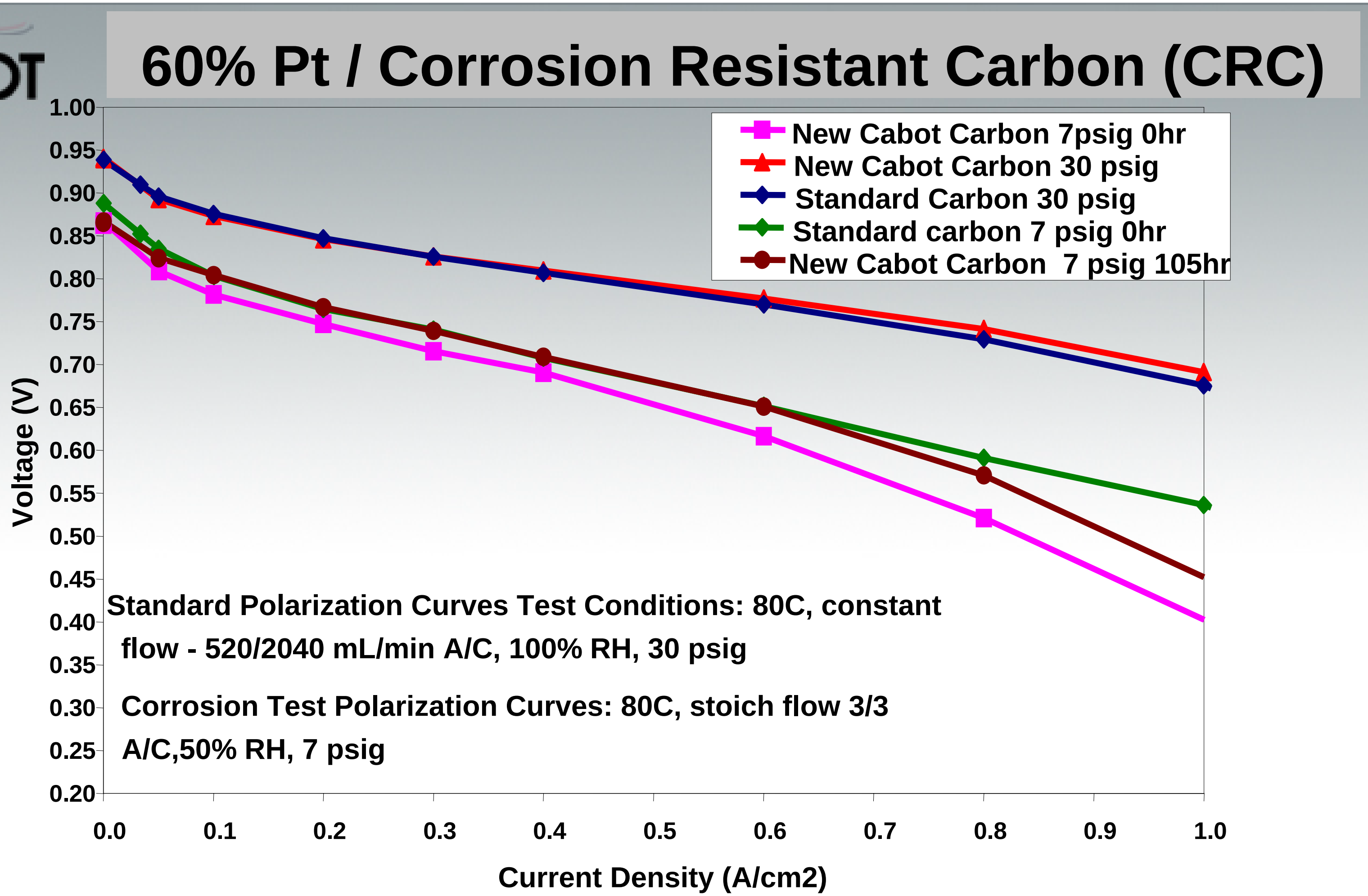
Superior Corrosion Resistance with New Cabot Carbon Support



- Identical initial absolute performance after layer optimization
- No loss of performance after 105 hrs corrosion test

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Summary

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- **Alloy Electrocatalysts:**
  - **Two fold mass activity improvement by Pt-alloy catalysts**
  - **High absolute performance combined with low precious metal loadings in a single cell and short stack**
  - **Significant durability improvement under cycling protocols**
- **New Carbon Supports:**
  - **Surface modification of carbon supports effectively enhances carbon corrosion resistance and enables operation at low relative humidity operating conditions**
  - **No performance loss after 105 hours of standard corrosion protocol without sacrificing initial performance**
- **Combination of durable Pt alloy catalysts with corrosion-resistant carbon supports is a viable way for next generation automotive fuel cell materials**

Future Work

- Cabot's press release on November13th,2006 announced plans to introduce new products in Q1, 2007:
  - **Superior Durability Electrocatalysts** based on Corrosion Resistant Carbon (CRC) supports
  - **Superior Performance Electrocatalysts** for Operation at Low Relative Humidity based on Modified Carbon Blacks (MCB)
- Further increase of specific and mass activity of alloys
- Integration of new alloys with durable carbon supports
- Additional information at www.cabot-corp.com
  - ECS meeting presentations on alloy catalysts, modified carbon blacks, and corrosion resistant carbons-based catalysts

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